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Description

The present invention relates to an electrodeposition coating film-forming composition capable of forming a coating film with varistor property and to an electrodeposition coating method using said composition. In detail, it relates to an electrodeposition coating method capable of forming a coating film which imparts high throwing property, corrosion resistance, and edge cover property, by electrodeposition coating an electrodeposition coating film-forming composition containing molybdenum disulphide powder as a first coating layer, said coating film having varistor property and being smooth and excellent in corrosion resistance, on which a second coating layer can be further provided by electrodeposition coating.

Hitherto, it has been considered to be difficult in principle to first provide deposits on a metal article to be coated by the electrodeposition coating method and after baking, further provide a second coating layer on the resulting coating film by electrodeposition coating because the first coating layer becomes electrically insulative.

However, in Japanese Patent Publication No. 24566/74, there is found an example of such two-layer electrodeposition by electrodeposition coating. The method of this Japanese Patent Publication No. 24566/74 is concerned with a method in which using black iron oxide as an essential component and an anionic electrodeposition paint composition as a vehicle, an article to be coated is subjected to electrodeposition coating and baked to form an electrically conductive coating film with marked properties regarding adhesive strength, electrical conductivity, surface characteristics, and corrosion resistance, and a second coating layer is further provided thereon by electrodeposition coating.

Furthermore, in Japanese Patent Kokai (Laid-Open) No. 51958/84, in order to improve the quality of the method of the aforesaid Japanese Patent Publication No. 24566/74, a coating film as a first coating layer is formed from a combination of a cationic electrodeposition paint composition with, as an electrically conductive substance, finely divided carbon, i.e., carbon black and/or graphite, whereby uniformity of the resulting coating film and high throwing property are attained, and in order to further improve the corrosion resistance, lead compounds such as, for example, lead silicate, lead chromate, lead acetate, or lead lactate are added.

British Patent GB 1,283,144 also discloses a method for two-layer electrodeposition using black iron oxide to impart electrical conductivity to the first coating layer.

As seen in the foregoing examples, in order to form an electrically conductive coating film by the electrodeposition coating method, the use of an electrically conductive substance is necessary. Up to date, black iron oxide, carbon black, graphite, and metal powder (e.g., zinc, copper) have been known as the electrically conductive substance.

However, in the case of using black iron oxide as an electrically conductive substance in an electrodeposition coating composition as in Japanese Patent Publication No. 24566/74, there is involved a defect that since black iron oxide has a high specific gravity and is used in the state of an aqueous solution in which the electrodeposition paint is diluted, the precipitability is very vigorous so that in the case that an article to be coated has a complicated shape, a uniform coating film in the respective portions is not formed.

Furthermore, in the case that carbon black and/or graphite which is finely divided carbon is used as an electrically conductive substance as in Japanese Patent Kokai (Laid-Open) No. 51958/84, since the electrodeposition coating is carried out by using a cationic electrodeposition paint composition but not an anionic electrodeposition paint composition, the corrosion resistance of a formed coating film is improved. However, since carbon black and/or graphite does not basically have rust resistivity, the electrodeposition paint is inferior to usual cationic electrodeposition paints free from carbon black and/or graphite in terms of the rust resistivity, i.e., corrosion resistance. Moreover, though it is described that in order to improve this corrosion resistance, it is preferable to add a lead compound, there is involved a defect that in the case that an electrically conductive electrodeposition paint contains such a substance(s) in an amount necessary for attaining the generally required corrosion resistance in cationic electrodeposition paints, the dispersion is difficult, and a uniform electrically conductive coating film is hardly obtained.

The present inventors have made extensive investigations in order to obtain a coating with superior uniformity and corrosion resistance and having high practical usage. As a result, it has been surprisingly found that an electrodeposition coating film-forming composition which forms a coating film with varistor property forms a smooth coating film with superior corrosion resistance and overcomes the above-described defects.

That is, the present invention relates to an electrodeposition coating film-forming composition capable of forming a coating film with varistor property which contains from 7 to 50 parts by weight of molybdenum disulphide powder per 100 parts by weight of the solids content. The present invention also relates to an

improved coating method which comprises forming a first electrodeposition coating layer on a metal article by electrodeposition coating with the above-described electrodeposition coating film-forming composition and then forming a second electrodeposition coating layer on the first electrodeposition coating layer by electrodeposition coating with the above-described electrodeposition coating film-forming composition or an anionic or cationic electrodeposition paint. In forming the above-described second electrodeposition coating layer, a voltage exceeding the varistor voltage of the first electrodeposition coating layer is applied.

The varistor property as referred to in the present invention means an electrical characteristic exhibiting nonlinear resistance sensitive to a change of the voltage. That is, it means a characteristic that when exceeding the critical voltage (varistor voltage), the resistance rapidly decreases to thereby flow a current.

Though coating films obtained by electrodeposition coating of paints containing conventional electrically conductive substances such as, for example, electrically conductive carbon black always exhibit electrical conductivity, the coating film with varistor property according to the present invention does not exhibit electrical conductivity at a voltage not higher than a specific voltage (varistor voltage) but exhibits it when exceeding the varistor voltage.

In more detail, in forming a first electrodeposition coating layer on a metal article to be coated by electrodeposition coating and further forming thereon a second electrodeposition coating layer by the use of an electrodeposition coating film-forming composition capable of forming a coating film with varistor property, which contains from 7 to 50 parts by weight of molybdenum disulphide powder per 100 parts by weight of the solids content, the present invention has the following characteristics. That is, the first electrodeposition coating layer with varistor property is formed first whilst an electrodeposition voltage exceeding the varistor voltage (critical voltage) is applied.

The content of molybdenum disulphide powder is from 7 to 50 parts by weight, preferably from 15 to 30 parts by weight, per 100 parts by weight of the solids content of the coating film-forming composition. If the content is less than 7 parts by weight, the electrical conductivity of a formed coating film is insufficient so that even when the voltage is increased, the second electrodeposition layer is not uniformly deposited. On the other hand, if it exceeds 50 parts by weight, the formed first electrodeposition layer causes surface roughening, resulting in undesirably affecting the finish of the second electrodeposition coating layer.

If desired, the electrodeposition coating film-forming composition according to the present invention can be incorporated with color pigments, extender pigments, or ultraviolet-resistant pigments, which have hitherto been used in electrodeposition paints, so far as they do not deteriorate the varistor property. Further, the composition may be incorporated with usual additives, activating agents, defoaming agents, or antioxidants.

As the main vehicle to be used in the electrodeposition coating film-forming composition according to the present invention, usual resins for electrodeposition coating can be used. Examples include resins for anionic electrodeposition coating such as epoxy resins, polyester resins, and acrylic resins; resins for cationic electrodeposition coatings; and resins for electrodeposition powder coating (EPC).

In undergoing the electrodeposition coating by the use of the electrodeposition coating film-forming composition of the present invention, the electrodeposition coating can be carried out under an electrodeposition coating condition of a direct current of from 50 to 500 V. After rinsing with water, the coating film is suitably dried at ordinary temperature of from 80 to 200°C for a period of from 10 to 30 minutes.

As the paint which can be used in the electrodeposition coating of the second coating layer according to the present invention, usual anionic or cationic electrodeposition paints and EPC can be used. Further, the above-described electrodeposition coating film-forming composition according to the present invention can again be used similarly. However, as described above, since in order to undergo the electrodeposition coating on the first coating layer to be formed, a current does not flow at a voltage not higher than the varistor voltage, a voltage exceeding the varistor voltage is used. Other conditions do not particularly change.

As described above, the first coating layer to be formed according to the present invention has a varistor property and, therefore, in forming a second coating layer, an initial current value is controlled, and the system is mild, whereby the second coating layer of superior smoothness can be formed.

On the other hand, a coating film formed on a first coating layer made of a conventional electrically conductive powder (such as carbon) has a high initial current value as seen in the usual electrodeposition coating and, therefore, the current is concentrated in the initial stage so that the smoothness of the coating film is inferior.

Furthermore, the molybdenum disulphide powder imparts a further superior corrosion resistance, thereby giving rise to a characteristic that superior corrosion resistance is obtainable even when a usual rust-resistant pigment is not used.

Also, the present invention exhibits the following superior characteristics. For example, since two-layer electrodeposition coating can be carried out by the usual two-layer electrodeposition coating, a high throwing property is obtained. However, since the two-stage current supply is carried out by applying the characteristic of varistor property, a higher throwing property is obtained. That is, in the case of undergoing the two-layer electrodeposition coating, if at the time of forming the first coating layer, the first coating layer is formed by electrodeposition coating at a voltage lower than the varistor voltage, portions which have not been completely coated are subsequently subjected to further electrodeposition coating so that the throwing property is improved. Thereafter, if a voltage of the varistor voltage or higher is applied at the time of forming the second coating layer, the second coating layer can be formed, whereby the total film thickness is improved. Thus, an increase of the film thickness which has never been seen in the past as well as a further improved throwing property can be obtained.

In accordance with the method of the present invention, the cover property in edge portions is improved, and an improved corrosion resistance in edge portions is obtained.

At present, in the field of electrodeposition coating for automobiles, in order to increase the rust resistivity, improvements and designs regarding the resins and paints are made. That is, with respect to the resins, by suppressing the flowability in the edge portions at the time of baking, the film thickness in the edge portions is intended to be ensured. With respect to the paints, by increasing the amount of a pigment, the flowability is depressed, whereby the coating film thickness in the edge portions is ensured, and by adding a rheology control agent, a similar action is made. However, in any of these cases, there are caused such problems that the flowability of the coating film is inferior and that the finish appearance is lowered.

On the other hand, according to the method of the present invention, the sharpness in the edge portions completely disappears by the electrodeposition coating for first coating layer, and the covering of the edge portions is readily carried out in the electrodeposition coating for second coating layer. Accordingly, in designing the paint, the electrodeposition coating can be achieved without difficulty, and the film thickness can be completely ensured, resulting in a great advantage that the corrosion from the edge portions is prevented.

In accordance with the present invention, a high film thickness is obtainable by electrodeposition coating. For example, in a three-coat electrodeposition system which is presently employed in automobile body coating, an intermediate coat can be omitted, and at a decrease of the number of process steps, prevention of pollution problems, and an improvement in productivity are obtainable.

Furthermore, an improvement of quality of electrodeposition paint is obtainable. For example, in the case of an anionic acrylic electrodeposition paint which is presently employed for the one-coat electrodeposition paint, the corrosion resistance is 120 to 240 hours in terms of the salt spray test. Further, though in a cationic acrylic electrodeposition paint, the quality of corrosion resistance is 480 hours, if the electrodeposition coating film-forming composition of the present invention is applied for the first coating layer by electrodeposition coating, and the cationic acrylic electrodeposition paint is applied for the second coating layer, a two-coat electrodeposition coating film having superior corrosion resistance and weathering resistance can be obtained. With conventional ones is obtained, whereby a great improvement in the corrosion resistance of acrylic electrodeposition coating film which has never been achieved can be attained.

Next, while the first coating layer is formed by the electrodeposition coating of the electrodeposition coating film-forming composition according to the present invention, the second coating layer is formed by the electrodeposition coating of the electrodeposition coating film-forming composition comparable to the usual electrodeposition coating film-forming composition. Thus, the electrodeposition coating film-forming composition is further applied to increase the film thickness, whereby the corrosion resistance is further improved.

Also, a usual cationic electrodeposition coating is applied to the second coating layer by electrodeposition coating, whereby not only the corrosion resistance but also various performances inherent thereto can be improved. Furthermore, the electrodeposition powder coating (EPC) as described in Japanese Patent Publication No. 585/76 can be applied as the second coating layer by electrodeposition coating, whereby the performances which EPC possesses can be improved. In the light of the above, the double coating method, which should be a revolutionary coating step with respect to the electrodeposition coating, can be practiced in various manners.

[EXAMPLES]

The present invention will be described with reference to Examples and Comparative Examples. In these examples, all parts and percents are by weight unless otherwise indicated.

EXAMPLE 1

Formulation of first component paste:

(1) Epoxy resin for cationic pigments dispersion ("MR-100" made by Shinto Paint Co., Ltd.; non-volatile matter content: 70%)	64.3 parts
(2) 88% Acetic acid aqueous solution	2.0 parts
(3) Butyl cellosolve	13.0 parts
(4) Molybdenum disulfide powder	167.0 parts
(5) Deionized water	160.0 parts

First of all, the aforesaid components (1) to (5) were mixed with 400 parts of glass beads having an average particle diameter of 2 mm, and the mixture was dispersed in a paint shaker for one hour so as to have a particle diameter of not more than 1 μ . Thereafter, the glass beads were removed by filtration to obtain a first component paste.

Formulation of second component resin solution:

(6) Resin for cationic electrodeposition coating film ("S-Via CED #700 Resin" made by Shinto Paint Co., Ltd.; non-volatile matter content: 72%) (blocked isocyanate-containing polyurethane-terminated polyethylene glycol-terminated diene-modified epoxy resin)	680.0 parts
(7) 88% Acetic acid aqueous solution	3.9 parts
(8) 50% Lactic acid aqueous solution	1.3 parts
(9) Propyl cellosolve	15.0 parts
(10) Deionized water	550.0 parts

Next, the resin for cationic electrodeposition coating film (6) was heated at 50 °C, and the acids (7) and (8) and propyl cellosolve (9) were added thereto with stirring. After keeping the mixture for one hour, the deionized water (10) was gradually added thereto with stirring to obtain a second resin solution.

Preparation of electrodeposition bath:

First component paste	352 parts
Second component resin solution	1549 parts
Deionized water	1410 parts

The aforesaid first component paste and second component resin solution were mixed, and the mixture was stirred to obtain an electrodeposition bath having a solids content of 20%.

Using this electrodeposition bath, an electrodeposition coating was carried out on a substrate, and then baked at 170 °C for 20 minutes to obtain a cured electrodeposition coating film.

Thereafter, the coating film was subjected to electrodeposition coating with, as an electrodeposition paint for second coating layer, a cationic electrodeposition paint ("S-Via CED #700 Gray" made by Shinto Paint Co., Ltd.) under the conditions shown in Table 1 below, rinsed with water, and then baked at 170 °C for 20 minutes to form a cured electrodeposition coating film. The coating film was smooth and uniform.

second component resin solution were mixed, and the mixture was stirred to obtain an electrodeposition bath having a solids content of 6.2.

An electrodeposition paint for first coating layer was prepared, and the conditions shown in Table 1 below, rinsed with water, in a 15 μ -thick good coating film.

Thereafter, the coating film was subjected to electrodeposition coating with, as an electrodeposition paint for second coating layer, a cationic electrodeposition paint ("S-Via CED #700 Gray" made by Shinto Paint Co., Ltd.) under the conditions shown in Table 1, rinsed with water, and then baked at 170 °C for 20 minutes to form a cured electrodeposition coating film having a thickness of 20 μ (total film thickness: 35 μ). The test results of this coating film are shown in Table 2.

EXAMPLES 2 TO 5

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Example	Parts of MoS ₂ per 100 parts of solids content
2	15
3	25
4	35
5	50

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The same procedures as in Example 1 were repeated, except that the amount of MoS₂ to be incorporated was changed as described above. Thus, four electrodeposition paints for first coating layer of Examples 2 to 5 having an MoS₂ content ranging from 15 to 50 parts per 100 parts of the solids content were prepared.

The respective electrodeposition paints for first coating layer had a solids content of 20% and a pH ranging from 6.1 to 6.4.

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Using each of these electrodeposition paints, electrodeposition coating was carried out under the conditions shown in Table 1 to prepare a coating film for first coating layer.

Next, using a cationic electrodeposition paint "S-Via CE" #700 Gray" as an electrodeposition paint for second coating layer, electrodeposition coating was carried out in the same manner as in Example 1 under the conditions shown in Table 1. Thus, the results shown in Table 2 were obtained.

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COMPARATIVE EXAMPLE 1

Black paste:

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(1) Resin for paint dispersion ("M10-100")	74.1 parts
(2) 68% Acetic acid aqueous solution	2.0 parts
(3) Butyl cellosolve	23.0 parts
(4) Carbon black	100.0 parts
(5) Deionized water	176.0 parts

35

The aforesaid components were mixed with 375 parts of glass beads having an average particle diameter of 2 mm, and the mixture was dispersed for 2 hours so as to have a particle diameter of 15 μ . Thereafter, the glass beads were removed by filtration to obtain a black paste.

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Preparation of electrodeposition bath:

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(6) Black paste as prepared	112.5 parts
(7) Second component dispersion (as in Example 1)	637.5 parts
(8) Deionized water	1250.0 parts

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The aforesaid black paste and second component resin solution were mixed, and the deionized water was then gradually added to the mixture with stirring to prepare an electrodeposition paint having a carbon black content of 10% in the total solids content. The electrodeposition paint had a solids content of 15% and a pH of 6.2.

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Using this electrodeposition paint, a phosphate-treated steel plate was subjected to electrodeposition coating for 3 minutes and baked at 170°C for 20 minutes to prepare a 15 μ -thick coating film for first coating layer.

While this coating film for first coating layer had a good appearance, it was not passed in the salt spray test for 480 hours.

Next, using "S-Via CE" #700 Gray" as an electrodeposition paint for second coating layer, a 15 μ -thick coating film for second coating layer was formed. While the appearance was good, the corrosion resistance for 840 hours and the

corrosion resistance in edge portion measured at 200 V for 3 minutes (it was found to be 19 cm. Further, when the electrodeposition was carried out at not higher than the varistor voltage (not higher than 150 V), the coverability of throwing property was found to be zero as shown in Table 2.

COMPARATIVE EXAMPLE 2

	Component	Parts
(1)	pigment dispersion	74.1
(2)	solvent and aqueous solution	2.0
(3)	colloidal silica	23.0
(4)	zinc phosphate	85.0
(5)	colloidal silica	15.0
(6)	deionized water	176.0

The aforesaid components were mixed to form a paint having a solids content of 15%.

Using this paint, a zinc phosphate film was electrodeposited at a bath temperature of 28°C and at 170 V for 3 minutes (under a condition of the film thickness of 15 μ). The resulting film was somewhat non-uniform with respect to the film surface state.

Next, using "S-Via CED #700" (a trade name), a second coating layer was formed. The appearance thereof reflected the distribution was somewhat non-uniform.

When subjected to the salt spray test, the corrosion resistance in edge portion was found to be 19.5 cm.

When the throwing property was measured at 210 V for 3 minutes (under a condition of the film thickness of 20 μ) by the Ford pipe method, it was found to be 19.5 cm. Further, when the electrodeposition for second coating layer was carried out at not higher than the varistor voltage (not higher than 150 V), the coverability of throwing property was found to be zero.

COMPARATIVE EXAMPLE 3

An electrodeposition bath was prepared in the same manner as in Example 1, except that the content of the molybdenum disulfide powder was reduced to 5 parts per 100 parts of the solids content. Using this electrodeposition bath, the same test as in Example 1 was carried out to obtain the results shown in Table 2. Because of too a small content of molybdenum disulfide powder, electrical conductivity was not obtained, and an electrodeposition coating film was not formed.

COMPARATIVE EXAMPLE 4

An electrodeposition bath was prepared in the same manner as in Example 1, except that the content of the molybdenum disulfide powder was reduced to 60 parts per 100 parts of the solids content. Using this electrodeposition bath, the same test as in Example 1 was carried out to obtain the results shown in Table 2. The resulting film surface caused a roughness and a defect in the finishing.

When the throwing property was measured at 210 V for 3 minutes (under a condition of the film thickness of 20 μ) by the Ford pipe method, it was found to be 19.5 cm. Further, when the electrodeposition for second coating layer was carried out at not higher than the varistor voltage (not higher than 150 V), the coverability of throwing property was found to be zero.

When the throwing property was measured at 210 V for 3 minutes (under a condition of the film thickness of 20 μ) by the Ford pipe method, it was found to be 19.5 cm. Further, when the electrodeposition for second coating layer was carried out at not higher than the varistor voltage (not higher than 150 V), the coverability of throwing property was found to be zero.

When the throwing property was measured at 210 V for 3 minutes (under a condition of the film thickness of 20 μ) by the Ford pipe method, it was found to be 19.5 cm. Further, when the electrodeposition for second coating layer was carried out at not higher than the varistor voltage (not higher than 150 V), the coverability of throwing property was found to be zero.

When the throwing property was measured at 210 V for 3 minutes (under a condition of the film thickness of 20 μ) by the Ford pipe method, it was found to be 19.5 cm. Further, when the electrodeposition for second coating layer was carried out at not higher than the varistor voltage (not higher than 150 V), the coverability of throwing property was found to be zero.

When the throwing property was measured at 210 V for 3 minutes (under a condition of the film thickness of 20 μ) by the Ford pipe method, it was found to be 19.5 cm. Further, when the electrodeposition for second coating layer was carried out at not higher than the varistor voltage (not higher than 150 V), the coverability of throwing property was found to be zero.

When the throwing property was measured at 210 V for 3 minutes (under a condition of the film thickness of 20 μ) by the Ford pipe method, it was found to be 19.5 cm. Further, when the electrodeposition for second coating layer was carried out at not higher than the varistor voltage (not higher than 150 V), the coverability of throwing property was found to be zero.

When the throwing property was measured at 210 V for 3 minutes (under a condition of the film thickness of 20 μ) by the Ford pipe method, it was found to be 19.5 cm. Further, when the electrodeposition for second coating layer was carried out at not higher than the varistor voltage (not higher than 150 V), the coverability of throwing property was found to be zero.

When the throwing property was measured at 210 V for 3 minutes (under a condition of the film thickness of 20 μ) by the Ford pipe method, it was found to be 19.5 cm. Further, when the electrodeposition for second coating layer was carried out at not higher than the varistor voltage (not higher than 150 V), the coverability of throwing property was found to be zero.

TABLE 1

(Electrodeposition Coating Condition)		
Coating Step		Coating Condition
1. Work article		CPC steel plate
2. Surface treatment		Bonderite #3020 treatment
3. Electrodeposition coating	1st coating layer)	Solids content: 20% (adjustment of solids content with deionized water) Voltage: 100 to 350 V Charge time: 3 minutes Bath temperature: $28 \pm 1^\circ\text{C}$ Film thickness: 15μ Water base: yes
Baking		20 minutes at 170°C
4. Electrodeposition coating	2nd coating layer)	Solids content: 20% Voltage: 150 to 400 V Charge time: 3 minutes Bath temperature: $28 \pm 1^\circ\text{C}$ Film thickness: 20μ Water base: yes
Baking		20 minutes at 170°C

TABLE 2

EXAMPLE No.				
1	2	3	4	5
Electrodeposition Paint for 1st Coating Layer				
10	15	25	35	50
Cationic Electrodeposition Paint for				

Electrodeposition coating film for 1st coating layer

Varistor property	found	found	found	found
Smoothness (appearance)	good	good	good	good
Film thickness (μm)	15	15	15	15
Corrosion resistance (480 hours)	passed	passed	passed	passed

Electrodeposition coating film for 2nd coating layer

Total film thickness (μm)	35	35	35	35
Smoothness (appearance)	uniform & good	uniform & good	uniform	good

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TABLE 2 (Cont'd.)

	EXAMPLE No.				
	1	2	3	4	5
	100/100	100/100	100/100	100/100	100/100
Impact resistance (150", 500 g)	passed	50	50	50	50
Corrosion resistance in planar portions (840 hours)	passed	passed	passed	passed	passed
Corrosion resistance in edge	3.4	2.1	0.6	1.2	2.3
Thermal property of electrodeposition paint for 1st coating layer	21.0	21.5	22.0	21.0	21.0
Voltage condition of electrodeposition paint for 2nd coating layer not higher than varistor voltage	1.0	2.0	3.0	3.0	3.0

TABLE 2 (Cont'd.)

Comparative EXAMPLE No.			
1	2	3	4
Electrodeposition Paint for 1st Coating Layer			
electrically			
conductive carbon	MoS ₂	MoS ₂	MoS ₂
10	10	5	60
Cationic Electrodeposition Paint for			
Cationic Electrodeposition Paint for			

1st coating layer	not found	not found	not found
Varistor property	good	rough	rough
Smoothness (appearance)	15	15	15
Film thickness (μm)	not passed	passed	passed
Corrosion resistance (480 hours)	35	33-37	35
Electrodeposition coating film for 2nd coating layer	good	rough in 1st coating layer	rough
Total film thickness (μm)			
Smoothness (appearance)			

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TABLE 2 (Cont'd.)

	Comparative EXAMPLE No.		
	1	2	3
Adhesion	100/100	100/100	100/100
Corrosion resistance in edge	20.5	10.8	2.4
Thickening property of electrodeposition paint for 1st coating layer	19.0	19.5	
Voltage condition of electrodeposition paint for 2nd coating layer not higher than varistor voltage	0	0	

[Note] In Comparative Example 3, no coating film was formed.

(1) Salt spray test:

(2) Throwing property:

(3) Corrosion resistance in edge : 3:

The corrosion resistance test is carried out in a manner in which the test is carried out for 120 hours by the salt spray test as defined by JIS Z 3101 and the number of pitting corrosions are read by using a magnifying glass. The numerical value is expressed as an average value of $n = 3$.

Using each of the electrodeposited plates of Examples 1 to 5 and Comparative Examples 1 to 4, a 0.3 x 100 x 100 mm steel plate is subjected to a surface treatment with Bonderite #3020 is subjected to electrodeposition of nickel under the conditions shown in Table 1, rinsed with water, and then baked. The thus coated plate is tested as a resistor with YHP1608A (made by Yokogawa-Hewlett-Packard, Ltd.) and examined for its varistor characteristic at an applied voltage in the range of from 0 to 100 V by means of a semiconductor analyzer ("YHP4145B" made by Yokogawa-Hewlett-Packard, Ltd.). Then, the varistor resistance is determined, and if it is less than 10⁷ ohm, it is determined to be not found.

(2) The film thickness of the electrodeposition coating film as a first coating layer (in the dry state) in the range of from 5 to 30 μm (preferably from 10 to 20 μm). Further, the film thickness of the electrodeposition coating film as a second coating layer (in the dry state) thereon is from 5 to 50 μm (preferably from 10 to 40 μm) in the case of the electrodeposition paints and from 5 to 200 μm in the case of the electrocoat paints.

The aforesaid pipes and electrodes were rinsed with water and baked at 170 °C for 20 minutes to form a cured electro-deposition.

In the MoS₂-containing portion of the first coating layer which has already been formed is electrically conductive, and the throwing property is not formed, and a covering property is not formed. On the other hand, in the case of using electrical deposition, the throwing property is not formed in the case of using electrical deposition, since the portion of the first coating layer where the coating film is not formed exhibits electrical conductivity, an electrodeposition coating film is formed superiorly in the portion, whereby no coverability of the throwing property is found.

(4) Improvement of the electrodeposition coating. A cutter blade having a surface treatment with Bonderite #3020 was subjected to electrodeposition coating. The electrodeposited coating was examined for the corrosion resistance in

edge portions. The results obtained

A coating film obtained

Accordingly, since in the edge coating, a special edge covering is required, on the other hand, in the case according to the present invention, the sharpness of the edges disappears by the electrodeposition coating, and the corrosion resistance in edge portions is good. (5) The finishing of the coating film of Example 3 and the top coat paint (a melamine-alkyd type) and two bake type (total thickness: 20 μ) having a top coat dispersion and three bake type (total thickness: 20 μ) provided therebetween.

EXAMPLE 6

An MoS_2 -containing anionic aqueous polybutadiene-modified electrodeposition paint for the first coating

Anionic electrodeposition pigment

- (1) Resin for pigment made by Shinto Paint Co., Ltd.
- (2) Triethylamine
- (3) Propyl cellosolve
- (4) Molybdenum

The aforesaid component (1) is a particle diameter of 2 mm, and the particle diameter of not more than 2 mm dispersion paste.

Preparation of electrodeposition bath

- (5) Dispersion paste
- (6) Resin for anionic electrodeposition made by Shinto Paint Co., Ltd.
- (7) Melamine resin made by Shinto Paint Co., Ltd.
- (8) Triethylamine
- (9) Deionized water

The aforesaid component (5) is a dispersion paste. After stirring for 30 minutes, the mixture was heated at higher than 50°C for 2 hours.

Thereafter, the mixture was cooled to room temperature, and the electrodeposition bath having a solid content of 20% was obtained.

Using the aforesaid electrodeposition bath, an electrodeposition coating was applied to a steel plate for 20 minutes. A thus formed coating film was dried at 170°C for 30 minutes and exhibited a good coated surface state.

in Table 2.

"CED #700 Gray" alone revealed a bad result as 25.8.

According to the present invention, it is impossible to undergo double electrodeposition coating, it is impossible to undergo double electrodeposition coating. On the other hand, in the case according to the present invention, the sharpness of the edges disappears by the electrodeposition coating, and the corrosion resistance in edge portions is good, whereby a corrosion-resisting effect of the coating film is good.

According to the present invention, a two-layer electrodeposited coating film (15 μ of the "CED #700 Gray"; total = 35 μ) having provided thereon a thickness of 30 μ was explicitly better than that of a two coat using a film made singly of "CED #700 Gray" (thickness: 30 μ) and the finish appearance of a three coat and an intermediate coat paint (an oil-free melamine-alkyd

type paint corresponding to "S-Via AED #300" using an electrodeposition paint made by Shinto Paint Co., Ltd., was used as an elec-

polybutadiene-modified anionic electrodeposition paint (solid content: 21.5%)	64.0 parts
	7.1 parts
	48.2 parts
	149.4 parts

The aforesaid component (1) is a dispersion paste. After stirring for 30 minutes, the mixture was heated at higher than 50°C for 2 hours. Thereafter, the mixture was cooled to room temperature, and the electrodeposition bath having a solid content of 20% was obtained.

(5) Dispersion paste	268 parts
(6) Resin for anionic electrodeposition made by Shinto Paint Co., Ltd.	399 parts
(7) Melamine resin made by Shinto Paint Co., Ltd.	7.7 parts
(8) Triethylamine	42.4 parts
(9) Deionized water	2854 parts

The aforesaid component (5) is a dispersion paste. After stirring for 30 minutes, the mixture was heated at higher than 50°C for 2 hours.

Thereafter, the mixture was cooled to room temperature, and the electrodeposition bath having a solid content of 20% was obtained.

Using the aforesaid electrodeposition bath, an electrodeposition coating was applied to a steel plate for 20 minutes. A thus formed coating film was dried at 170°C for 30 minutes and exhibited a good coated surface state.

Using "S-Via CED #700" spray coating. As a result, a 20 μ -thick coating was obtained of good quality.

- This coating film was subjected to salt spray test. As a result, both of the electrodeposition coating film as first coating layer (15 μ) and the electrodeposition coating film as second coating layer (35 μ) were passed at 360 hours and 840 hours, respectively.

EXAMPLE 7

- Using the MoS₂-containing electrodeposition coating film as first coating layer and the electrodeposition paint ("S-Via AEC #108" made by Shinto Paint Co., Ltd.), a second coating layer was provided thereon by electrodeposition coating at a bath temperature of 28°C and at 250 V for 3 minutes and baked at 170°C for 20 minutes to obtain a coating film having a film thickness of 20 μ .

- On the other hand, a steel plate was subjected to electrodeposition coating with an AED #300 electrodeposition paint at a bath temperature of 28°C and at 200 V for 3 minutes and baked at 170°C for 20 minutes to obtain a coating film having a film thickness of 20 μ .

- These coating films were subjected to salt spray test. As a result, both of the coating film made singly of AED #300 (20 μ) and the electrodeposition coating film (35 μ) were passed at 360 hours and 840 hours, respectively.

EXAMPLE 8

- Using the MoS₂-containing electrodeposition coating film as first coating layer and the electrodeposition paint ("Bonderite #1077" made by Shinto Paint Co., Ltd.), a second coating layer was provided thereon by electrodeposition coating at a bath temperature of 28°C and at 250 V for 3 minutes and baked at 170°C for 20 minutes to obtain a coating film having a film thickness of 20 μ of good quality.

- On the other hand, a steel plate was subjected to electrodeposition coating with an AED #108 at a bath temperature of 28°C and at 200 V for 3 minutes and baked at 170°C for 20 minutes to obtain a coating film having a film thickness of 20 μ .

- These coating films were subjected to salt spray test. As a result, both of the coating film made singly of AED #108 (20 μ) and the electrodeposition coating film (35 μ) were passed at 240 hours and 720 hours, respectively.

EXAMPLE 9

- Using the MoS₂-containing electrodeposition coating film as first coating layer and the electrodeposition paint ("Bonderite #1077" made by Shinto Paint Co., Ltd.), a second coating layer was provided thereon by electrodeposition coating at a bath temperature of 28°C and at 250 V for 3 minutes and baked at 170°C for 20 minutes to obtain a coating film having a film thickness of 20 μ of good quality.

- On the other hand, a steel plate was subjected to electrodeposition coating with an AED #108 at a bath temperature of 28°C and at 200 V for 3 minutes and baked at 170°C for 20 minutes to obtain a coating film having a film thickness of 20 μ .

- These coating films were subjected to salt spray test. As a result, both of the coating film made singly of CED #1000 (20 μ) and the electrodeposition coating film (35 μ) were passed at 480 hours and 840 hours, respectively.

EXAMPLE 10

Using the MoS₂-containing electrodeposition coating film as first coating layer and the electrodeposition paint ("Bonderite #1077" made by Shinto Paint Co., Ltd.), a second coating layer was provided thereon by electrodeposition coating at a bath temperature of 28°C and at 250 V for 3 minutes and baked at 170°C for 20 minutes to obtain a coating film having a film thickness of 20 μ of good quality.

On the other hand, a steel plate was subjected to electrodeposition coating with an AED #108 at a bath temperature of 28°C and at 200 V for 3 minutes and baked at 170°C for 20 minutes to obtain a coating film having a film thickness of 20 μ .

These coating films were subjected to salt spray test. As a result, both of the electrodeposition coating film as first coating layer (15 μ) and the electrodeposition coating film as second coating layer (35 μ) were passed at 360 hours and 840 hours, respectively.

On the other hand, a steel plate was subjected to electrodeposition coating with an AED #300 electrodeposition paint at a bath temperature of 28°C and at 200 V for 3 minutes and baked at 170°C for 20 minutes to obtain a coating film having a film thickness of 20 μ .

These coating films were subjected to salt spray test. As a result, both of the coating film made singly of AED #300 (20 μ) and the electrodeposition coating film (35 μ) were passed at 360 hours and 840 hours, respectively.

On the other hand, a steel plate was subjected to electrodeposition coating with an AED #108 at a bath temperature of 28°C and at 200 V for 3 minutes and baked at 170°C for 20 minutes to obtain a coating film having a film thickness of 20 μ .

These coating films were subjected to salt spray test. As a result, both of the coating film made singly of AED #108 (20 μ) and the electrodeposition coating film (35 μ) were passed at 240 hours and 720 hours, respectively.

On the other hand, a steel plate was subjected to electrodeposition coating with an AED #108 at a bath temperature of 28°C and at 200 V for 3 minutes and baked at 170°C for 20 minutes to obtain a coating film having a film thickness of 20 μ .

On the other hand, a steel plate was subjected to electrodeposition coating with an AED #108 at a bath temperature of 28°C and at 200 V for 3 minutes and baked at 170°C for 20 minutes to obtain a coating film having a film thickness of 20 μ .

On the other hand, a steel plate was subjected to electrodeposition coating with an AED #108 at a bath temperature of 28°C and at 200 V for 3 minutes and baked at 170°C for 20 minutes to obtain a coating film having a film thickness of 20 μ .

These coating films were subjected to salt spray test. As a result, both of the coating film made singly of CED #1000 (20 μ) and the electrodeposition coating film (35 μ) were passed at 480 hours and 840 hours, respectively.

On the other hand, a steel plate was subjected to electrodeposition coating with an AED #108 at a bath temperature of 28°C and at 200 V for 3 minutes and baked at 170°C for 20 minutes to obtain a coating film having a film thickness of 20 μ .

5 These coating films were prepared by electroplating. As a result, they were passed at 1000 hours.
 In the light of the above, it can be seen that with the present invention, an electrodeposition coating film with
 varistor property is obtainable, not only that positive to undergo two-layer electrodeposition
 coating, but also superior properties such as high adhesion property, high corrosion resistance, and
 edge corner property are obtained. Furthermore, it is possible to undergo multistage electrodeposition
10 coating, and a coating film with excellent corrosion resistance can be obtained.
 Moreover, since there are various methods such as an electrolytic method that a coating system by the multicoat
 coating mode which has been known in the prior art, the present invention can be achieved like
 the usual coating, the present invention can be widely applied in the various industrial
 coating areas.

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Revendications

1. Composition filmogène capable de former un film de revêtement ayant une propriété de revêtement, qui contient 10 à 20 parties en poids de poudre de disulfure de molybdène pour 1 partie en poids de sulfure de cadmate continu solide.
2. Procédé de revêtement sur un article métallique de revêtement par électrodeposition avec une composition filmogène, qui consiste à former une première couche de revêtement par électrodeposition avec une composition filmogène selon la revendication 1, puis à former une seconde couche de revêtement par électrodeposition avec une composition filmogène selon la revendication 1.
3. Procédé de revêtement sur un article métallique de revêtement par électrodeposition, qui consiste à former une première couche de revêtement par électrodeposition avec une composition filmogène de revêtement selon la revendication 1, puis à former une seconde couche de revêtement par électrodeposition par électrodeposition anionique ou cationique.
4. Procédé de revêtement de revêtement par électrodeposition, qui consiste à former une première couche de revêtement par électrodeposition, puis à former une seconde couche de revêtement par électrodeposition, en appliquant une tension supérieure à la tension critique.

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